Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Reduced roughness for improved mobility in benzodipyrrolidone-based, *n*-type OFETs

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Supporting Information

General experimental

Instrumental

NMR spectra were recorded on a Bruker DPX0 400 MHz spectrometer using an internal deuterium lock at ambient probe temperatures unless stated otherwise. Chemical shifts (δ) are quoted in ppm relative to the solvent residual peak, with peak multiplicity (bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration and coupling constants *(J)* quoted in Hz (uncorrected) as appropriate. $CDCl_3$ was used as the solvent for all spectra unless stated otherwise. Proton solvent residual peaks are taken as: 7.26 for $CDCl_3$, 7.15 for C_6D_6, 3.34 for methanol-d_4, 2.52 for DMSO-d_6; and carbon solvent residual peaks as: 77.16 for $CDCl_3$, 128.6 for C_6D_6, 49.9 for methanol-d_4, 39.7 for DMSO-d_6. ***Infrared spectra*** were recorded using an FTIR spectrometer as evaporated films or neat using NaCl or KBr windows. ***Mass spectra*** were recorded by the Imperial College London Department of Chemistry Mass Spectrometry Service on a Micromass Platform II or AutoSpec-Q spectrometer. ***Microwave chemistry*** was performed in a Biotage initiator v.2.3; the desired reaction temperature was set and the microwave power automatically applied and varied accordingly to achieve this. ***Molecular weights*** (Number-average [M_n] and weight-average [M_w]) were recorded on an Agilent Technologies 1200 series GPC in chlorobenzene at 80°C, using two PL mixed B columns in series, calibrated against narrow polydispersity polystyrene standards. ***Thermal gravimetric analysis (TGA)*** plots were obtained with a Perkin Elmer Pyris 1 TGA. ***Differential scanning calorimetry (DSC)*** experiments were carried out on a TA Instruments DSC Tzero Q20 instrument. ***X-ray diffraction (XRD)*** measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu K α 1 beam and a X' CELERATOR detector, using a current of 40 mA and an accelerating voltage of 40 kV; films were drop-cast from polymer solution (10 mg/mL in hot chlorobenzene) onto an Si substrate and allowed to dry in air for 24 h. ***UV-Vis detection*** was performed using a UV-1601 Shimadzu UV-Vis spectrometer. ***Ionisation potentials*** were evaluated by Photo-electron Spectroscopy in Air (PESA) on a Riken Keiki AC-2 PESA spectrometer. PESA samples were prepared by spin-coating polymer thin-films on glass substrates from 1 mg/mL solutions in chlorobenzene and were run with a light intensity of 5 nW and data processed with a power number of 0.5. ***Atomic force microscopy (AFM)*** was performed on an Agilent 5500 instrument in tapping mode on thin-films akin to transistor devices with surface roughness measurements performed *in situ*. ***Computational models*** were produced using density functional theory (DFT) in Gaussian 09 software at the B3LYP/6-31G* basis set theory level with *N*-methyl substitution, for trimers or tetramers depending on the size of the system. For clarity hydrogens are typically omitted in visualising results.

Synthetic experimental procedures

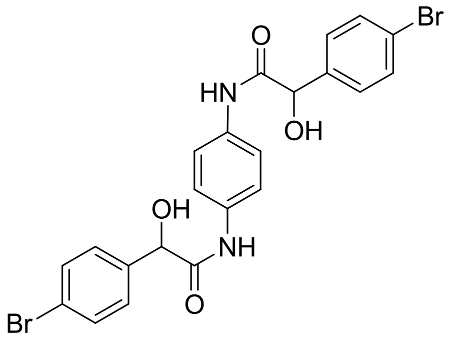
Detailed synthetic experimental procedures are described below. All solvents, reagents and other chemicals were used as received from commercial sources unless stated otherwise. The use of anhydrous chemicals infers anhydrous conditions under an argon or nitrogen atmosphere. Glassware for inert atmosphere reactions was oven dried and cooled under a flow of nitrogen. All temperatures – other than room temperature – are recorded as bath temperatures of the reaction, unless stated otherwise. Merck aluminium backed precoated silica gel (50 F254) plates were used for thin-layer chromatography (TLC). Visualisation was by ultraviolet light (254 nm). Column chromatography was performed on Merck silia gel (Merck 9385 Kieselgel 60, 230-400 mesh) under a positive air pressure using reagent grade solvent as received. DMF refers to dimethylformamide. The synthesis of the phenyl-flanked benzodipyrrolidone-based (**BPP**) copolymers by palladium catalyzed cross-coupling methodology is shown in Scheme S1.

Organic field-effect transistor (OFET) device fabrication

Top-gate, bottom-contact devices were fabricated on 2x2 cm glass substrates under an inert atmosphere (nitrogen glovebox). Glass slides are cleaned in a DECON90 DI-Water solution, DI-water, acetone and isopropanol for 10 minutes each in an ultrasonic bath then dried under nitrogen gas flow. To help with the adhesion of the gold 2 nm of aluminium is evaporated before putting 25 nm of gold down. Polymer thin-films were spin-coated from 5 mg/mL solution in hot (75 °C) *ortho*-dichlorobenzene at 2000 rpm for 30 s then dried at 100 °C for 10 min. A perfluorinated polymer (commercial name CYTOP from Ashani Glass) is used as the gate dielectric and applied via spin-coating at 2000 rpm for 60 s and curing at 100 °C for 30 min. 50 nm Aluminium is evaporated on top of the dielectric as the gate electrode.

Detailed Synthetic Procedures

1,4-Bis(α-hydroxy(4-bromophenyl)acetylamino)benzene



The compound was prepared according to the literature.[1] A mixture of *p*-phenylenediamine (3.12 g, 28.9 mmol) and 4-bromo-DL-mandelic acid (20.0 g, 86.6 mmol) in chlorobenzene (100 mL) was stirred at 130 °C for 18 hours. On cooling to room temperature the resulting precipitate was filtered off, washed with ethanol and dried under high vacuum to afford the title compound as a white solid (13.0 g, 85%). The NMR spectra were in agreement with those previously reported for the compound.

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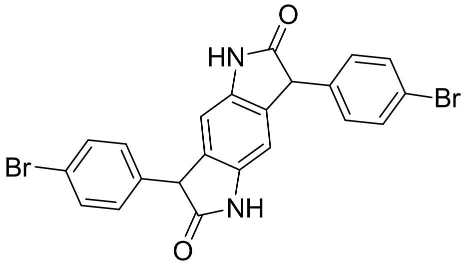
[1] Cui, W.; Yuen, J.; Wudl, F. *Macromolecules* **2011**, *44*, 7869.

3,7-Di(4-bromophenyl)-2,6-dioxo-1,2,3,4,5,6,7-hexahydrobenzo[1,2-*b*:4,5-*b'*]dipyrrole



The compound was prepared according to the literature.[2] To 1,4-bis(α-hydroxy(4-bromophenyl)acetylamino)benzene (13.00 g, 24.40 mmol) was added concentrated sulfuric acid (125 mL) and the mixture stirred at room temperature for 16 hours, then poured into ice water. The resulting precipitate was filtered off, washed with water and dried in air to afford the title compound as a light brown solid (11.62 g, 96%). The NMR spectra were in agreement with those previously reported for the compound.

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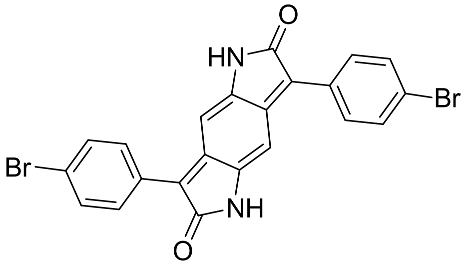
[2] Cui, W.; Yuen, J.; Wudl, F. *Macromolecules* **2011**, *44*, 7869.

3,7-Di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b'*]dipyrrole



The compound was prepared according to the literature.[3] Aqueous sodium hydroxide solution (5N) (8.40 mL, 42.01 mmol) was added dropwise to a suspension of 3,7-di(4-bromophenyl)-2,6-dioxo-1,2,3,4,5,6,7-hexahydrobenzo[1,2-*b*:4,5-*b'*]dipyrrole (11.57 g, 23.34 mmol) in ethanol (100 mL). Then potassium persulfate (16.97 g, 62.78 mmol) in water (56 mL) was added and the mixture heated at reflux for 2 h. On cooling to room temperature, the resulting precipitate was filtered off, washed with water, ethanol and acetone and dried under high vacuum to afford the title compound as a brown solid (11.53 g, quant.). The spectra were in agreement with those previously reported for the compound.

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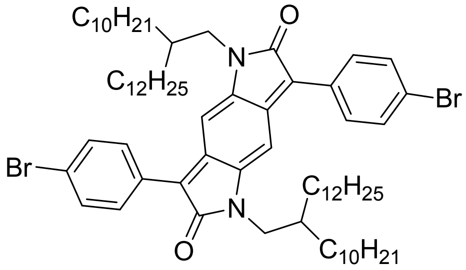
[3] Cui, W.; Yuen, J.; Wudl, F. *Macromolecules* **2011**, *44*, 7869.

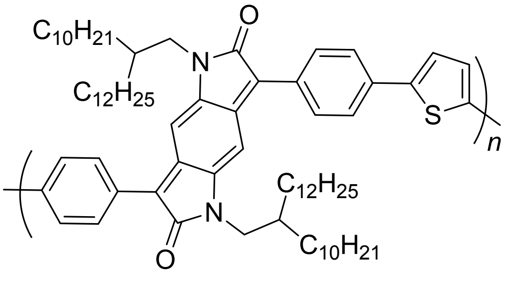
N,N'-Di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b'*]dipyrrole



To a mixture of 3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b'*]dipyrrole (5.00 g, 10.12 mmol) and potassium carbonate (5.60 g, 40.49 mmol) in anhydrous DMF (90 mL) was added 2-decyltetradecanyl bromide (18.81 g, 40.49 mmol). After stirring for 16 h at 80 °C, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting in 1:2 hexane/dichloromethane to afford the title compound as a dark red-brown solid (5.02 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.83-0.91 (m, CH_3, 12H), 1.14-1.37 (m, CH_2, 80H), 1.76 (m, C*H*, 2H), 3.50 (d, J = 7.1 Hz, NCH_2, 4H), 6.29 (s, Ar*H*, 2H), 7.55-7.64 (m, Ar*H*, 8H); ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 14.28, 22.85, 26.83, 29.51, 29.82, 30.15, 31.89, 32.07, 37.25, 44.16, 97.31, 123.74, 126.48, 130.17, 131.08, 132.20, 134.63, 144.45, 169.71. MS *m/z* (MALDI TOF LD$^+$): calculated 1169.68 ([M+H]$^+$), found 1169.86.

See **Spectrum S1** for proton NMR spectrum.

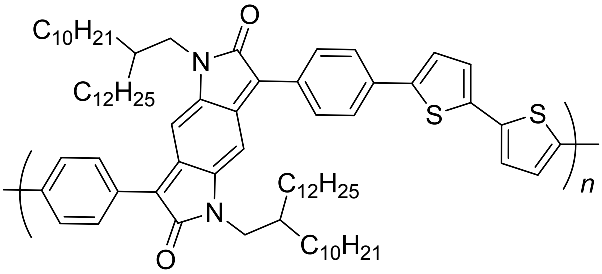
BPP-T



C10C12-BPP-T

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (250 mg, 0.21 mmol), 2,5-bis(trimethylstannyl)thiophene (88 mg, 0.21 mmol) and 2 mol% of tetrakis(triphenylphosphine)palladium(0). The vial was then sealed, *o*-xylene (0.50 mL) added, the mixture degassed for 30 minutes and submitted to the microwave reactor for: 2 minutes at 120 and 150 °C then 40 minutes at 170 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with methanol, acetone, hexane and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark blue solid (99 mg, 41 % yield, chloroform fraction). M_n = 25 kDa, M_w = 41 kDa, PDI = 1.64.

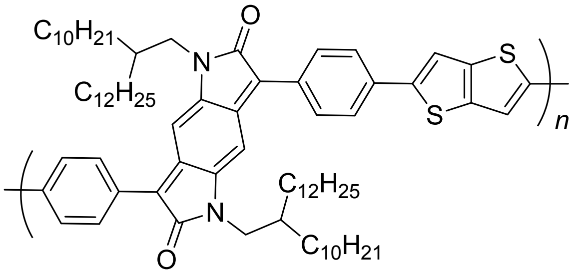
BPP-2T



C10C12-BPP-2T

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (250 mg, 0.21 mmol), 2,5-5,5'-bis(trimethylstannyl)-2,2'-bithiophene (105 mg, 0.21 mmol) and 2 mol% of tetrakis(triphenylphosphine)palladium(0). The vial was then sealed, *o*-xylene (0.50 mL) added, the mixture degassed for 30 minutes and submitted to the microwave reactor for: 2 minutes at 120 and 150 °C then 40 minutes at 170 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with methanol, acetone, hexane, chloroform and chlorobenzene. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark blue solid (39 mg, 15 % yield, chlorobenzene fraction). M_n = 17 kDa, M_w = 42 kDa, PDI = 2.47.

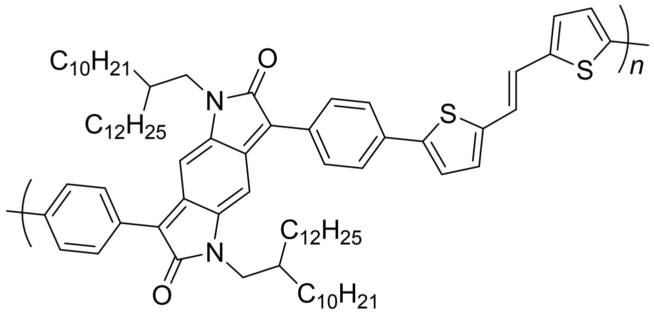
BPP-TT



C10C12-BPP-TT

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (250 mg, 0.21 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (100 mg, 0.21 mmol) and 2 mol% of tetrakis(triphenylphosphine)palladium(0). The vial was then sealed, *o*-xylene (0.50 mL) added, the mixture degassed for 30 minutes and submitted to the microwave reactor for: 2 minutes at 120 and 150 °C then 40 minutes at 170 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with methanol, acetone, hexane, chloroform and chlorobenzene. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark blue solid (123 mg, 49 % yield, chloroform fraction). M_n = 15 kDa, M_w = 51 kDa, PDI = 3.41.

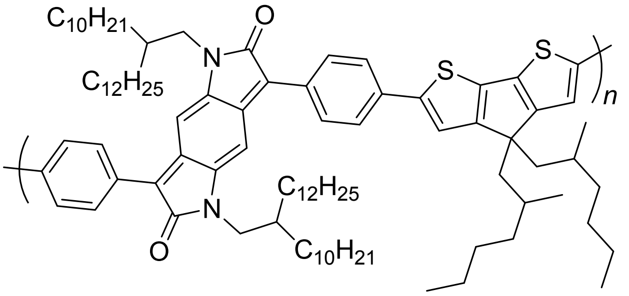
BPP-TVT



C10C12-BPP-TVT

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (200 mg, 0.17 mmol), (*E*)-1,2-bis(5-trimethylstannyl)thiophen-2-yl-ethene (89 mg, 0.17 mmol), 2 mol% of tris(dibenzylideneacetone)dipalladium(0) and 8 mol% of triphenylphosphine. The vial was then sealed, toluene/DMF (10:1) (3.30 mL) added, the mixture degassed for 30 minutes, sealed under argon and stirred vigorously for 16 hours at 110 °C in the dark. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark blue solid (32 mg, 16 % yield, chloroform fraction). M_n = 20 kDa, M_w = 46 kDa, PDI = 2.28.

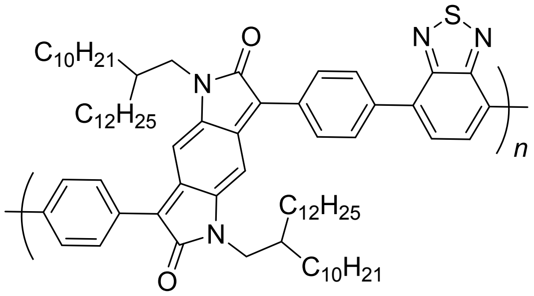
BPP-CPDT



C10C12-BPP-CPDT

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (156 mg, 0.13 mmol), 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-*b*:3,4-*b*']dithiophene (264 mg, 0.38 mmol), 4 mol% of tris(dibenzylideneacetone)dipalladium(0) and 16 mol% of triphenylphosphine. The vial was then sealed, toluene/DMF (10:1) (10 mL) added, the mixture degassed for 30 minutes, sealed under argon and stirred vigorously for 5 days at 110 °C in the dark. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with methanol, acetone, hexane and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark black solid (66 mg, 36 % yield, chloroform fraction). M_n = 21 kDa, M_w = 41 kDa, PDI = 1.96.

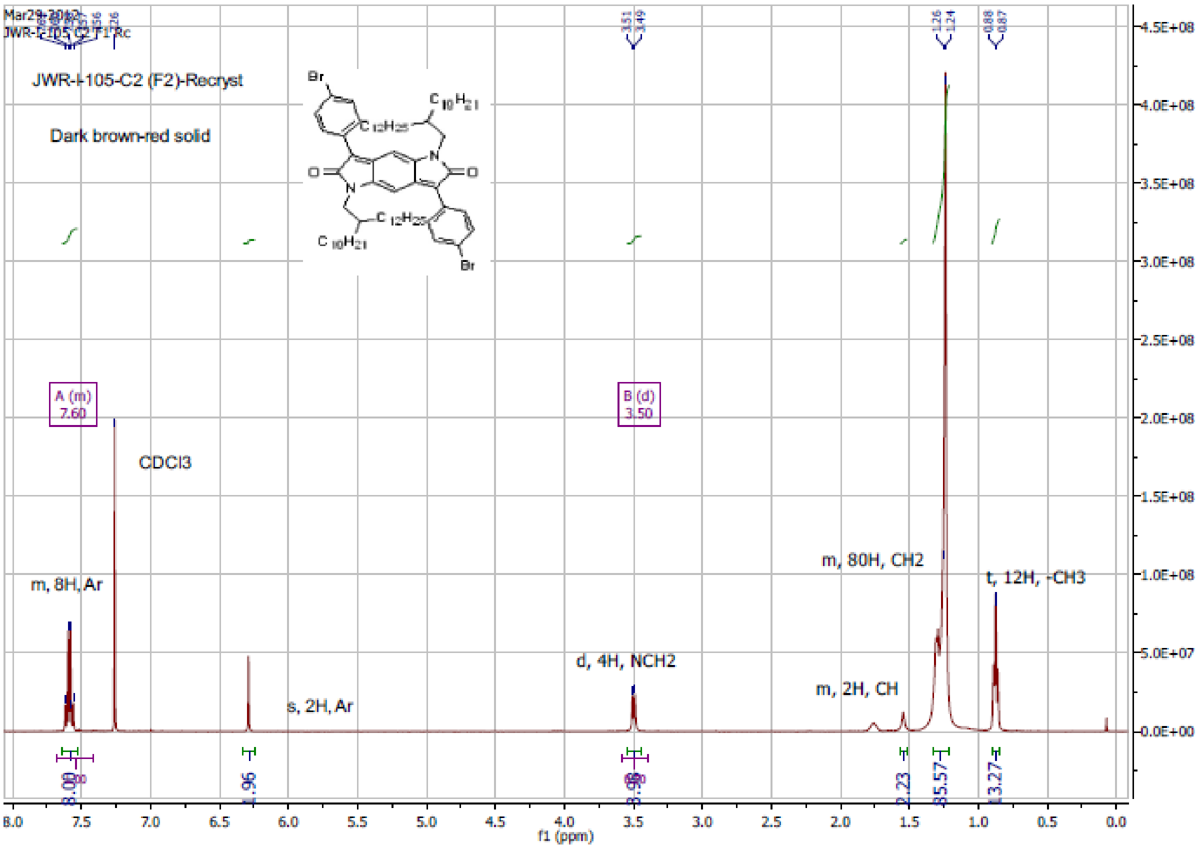
BPP-BT



C10C12-BPP-BT

A microwave vial was charged with *N,N'*-di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (116 mg, 0.10 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (38 mg, 0.10 mmol), 5 mol% of tris(dibenzylideneacetone)dipalladium and 10 mol% of triphenylphosphine and sealed. A degassed solution of Aliquat 336 (two drops) in toluene (1.50 mL) was then added, followed by a degassed aqueous solution (0.30 mL) of potassium phosphate tribasic (90 mg, 0.42 mmol). After degassing for a further 30 minutes the sealed mixture was stirred vigorously at 115 °C for 3 days in the dark under argon. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark purple solid (85 mg, 75% yield, chloroform). M_n = 54 kDa, M_w = 66 kDa, PDI = 1.23.

Additional Spectra



Spectrum S1. Proton NMR (400MHz, $CDCl_3$) spectrum of the dibrominated **BPP monomer** (*N,N'*-Di(2-decyltetradecanyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole).

Additional Figures

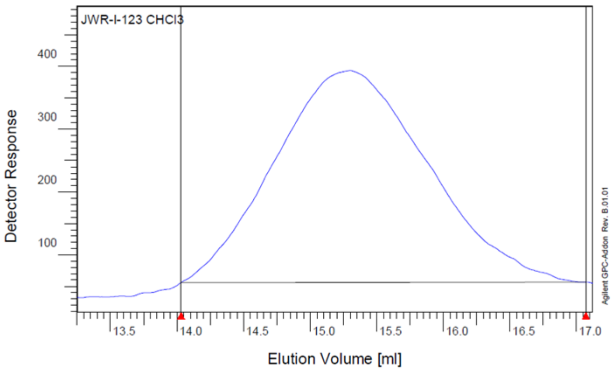


Figure S1. GPC trace of **BPP-T**, M_n = 25 kDa, M_w = 41 kDa, PDI = 1.64 (chloroform soxhlet fraction).

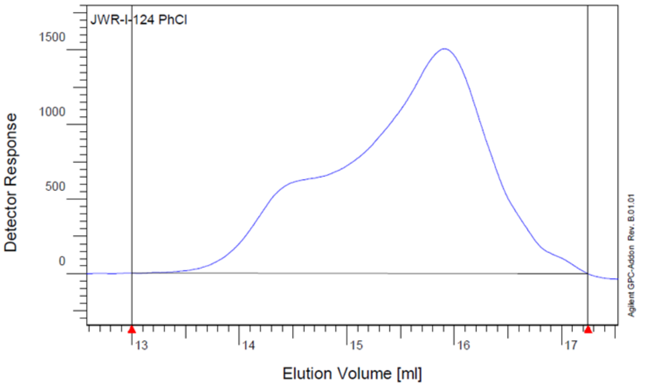


Figure S2. GPC trace of **BPP-2T**, M_n = 17 kDa, M_w = 42 kDa, PDI = 2.47 (chlorobenzene soxhlet fraction).

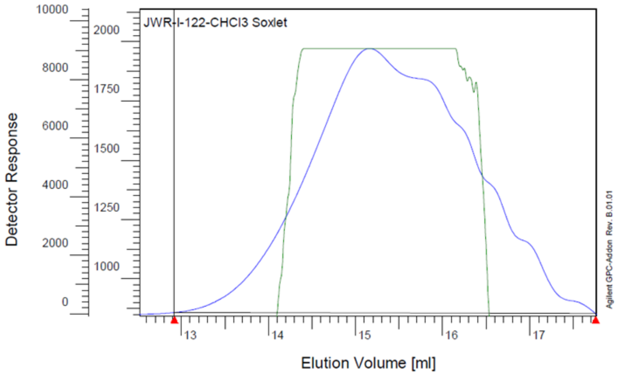


Figure S3. GPC trace of **BPP-TT**, M_n = 15 kDa, M_w = 51 kDa, PDI = 3.41 (chloroform soxhlet fraction).

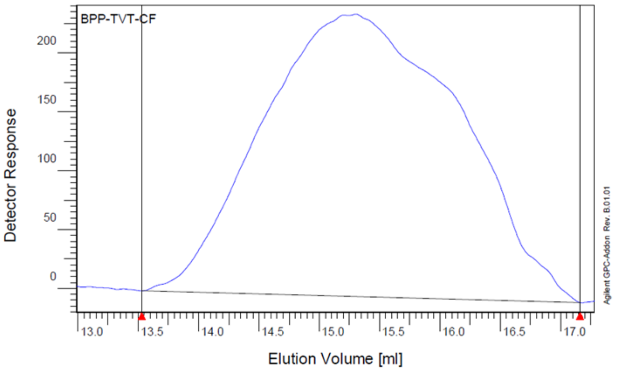


Figure S4. GPC trace of **BPP-TVT**, M_n = 20 kDa, M_w = 46 kDa, PDI = 2.28 (chloroform soxhlet fraction).

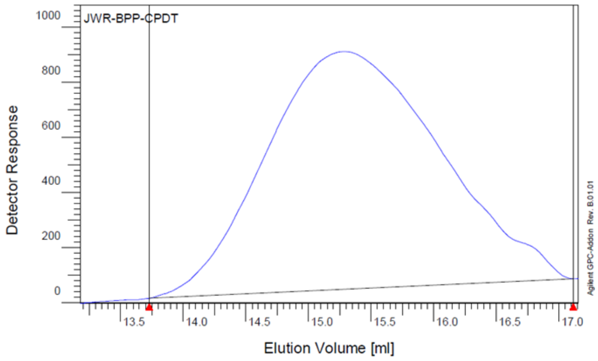


Figure S5. GPC trace of **BPP-CPDT**, M_n = 21 kDa, M_w = 41 kDa, PDI = 1.96 (chloroform soxhlet fraction).

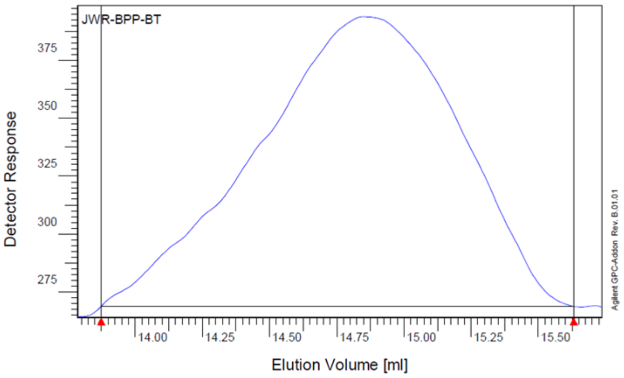


Figure S6. GPC trace of **BPP-BT**, M_n = 54 kDa, M_w = 66 kDa, PDI = 1.23 (chloroform soxhlet fraction).

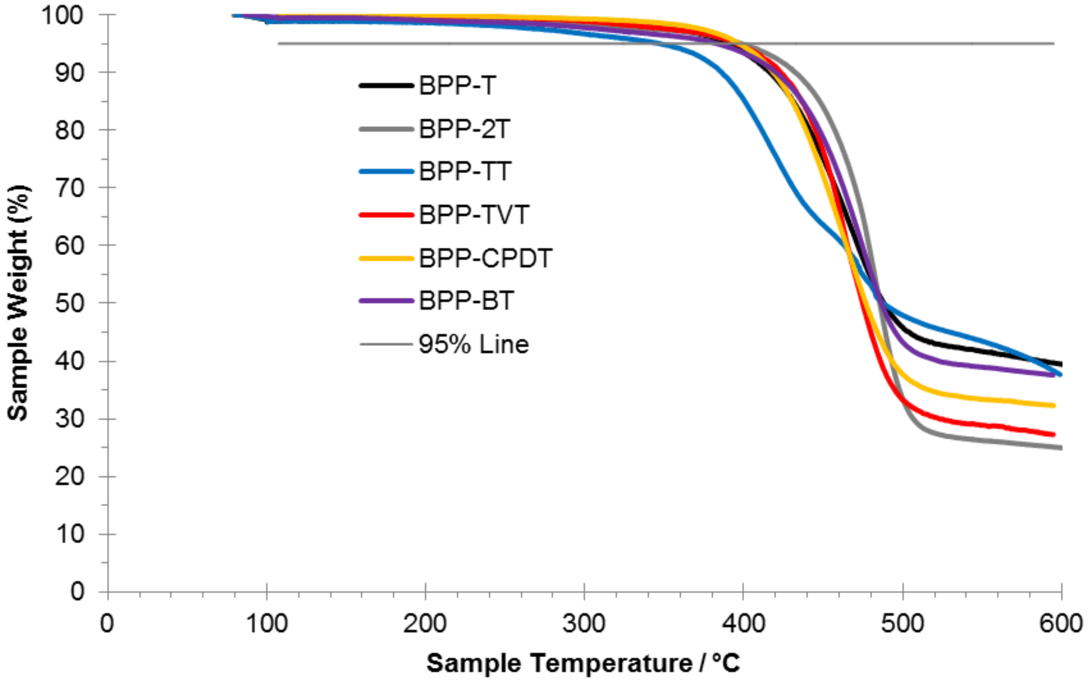


Figure S7. Thermogravimetric analysis (TGA) curves of the **BPP**-based copolymers (under a nitrogen atmosphere with a heating rate of 10 °C/min).

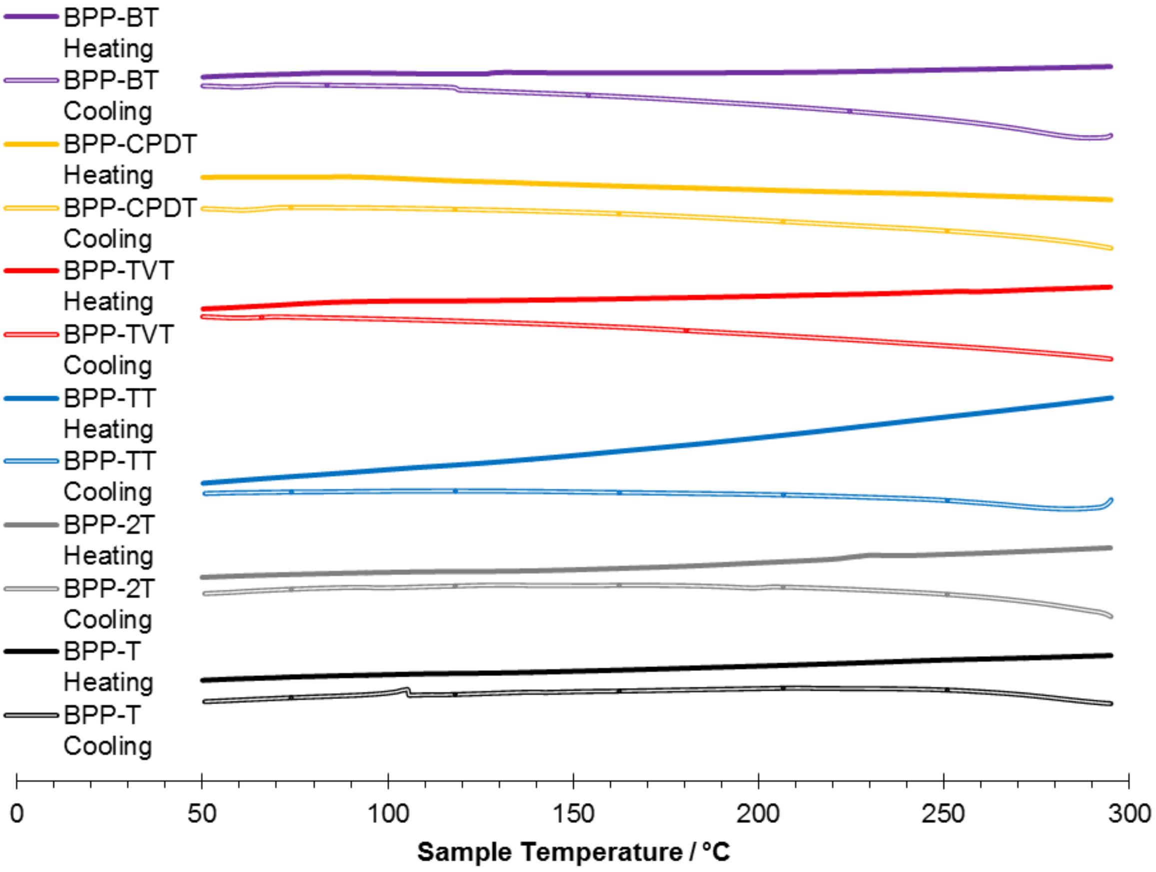


Figure S8. Differential scanning calorimetry (DSC) scans of the **BPP**-based copolymers (-30 to 200 °C, under a nitrogen atmosphere with a heating rate of 10 °C/min).

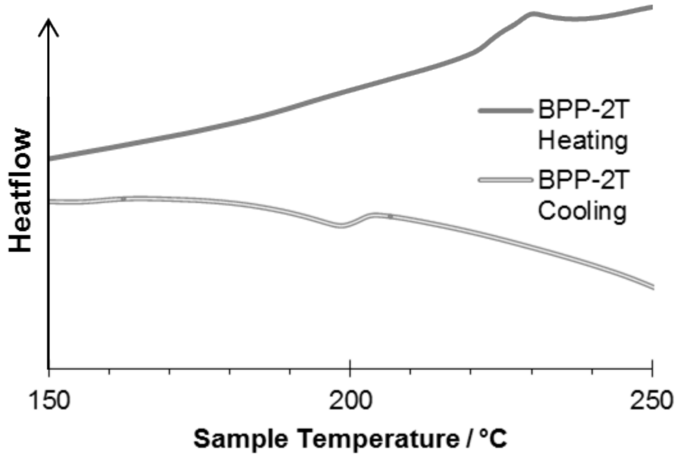


Figure S9. Differential scanning calorimetry (DSC) curve for the benzodipyrrolidone-based copolymer **BPP-2T** (-30 to 200 °C, under a nitrogen atmosphere with a heating rate of 10 °C/min).

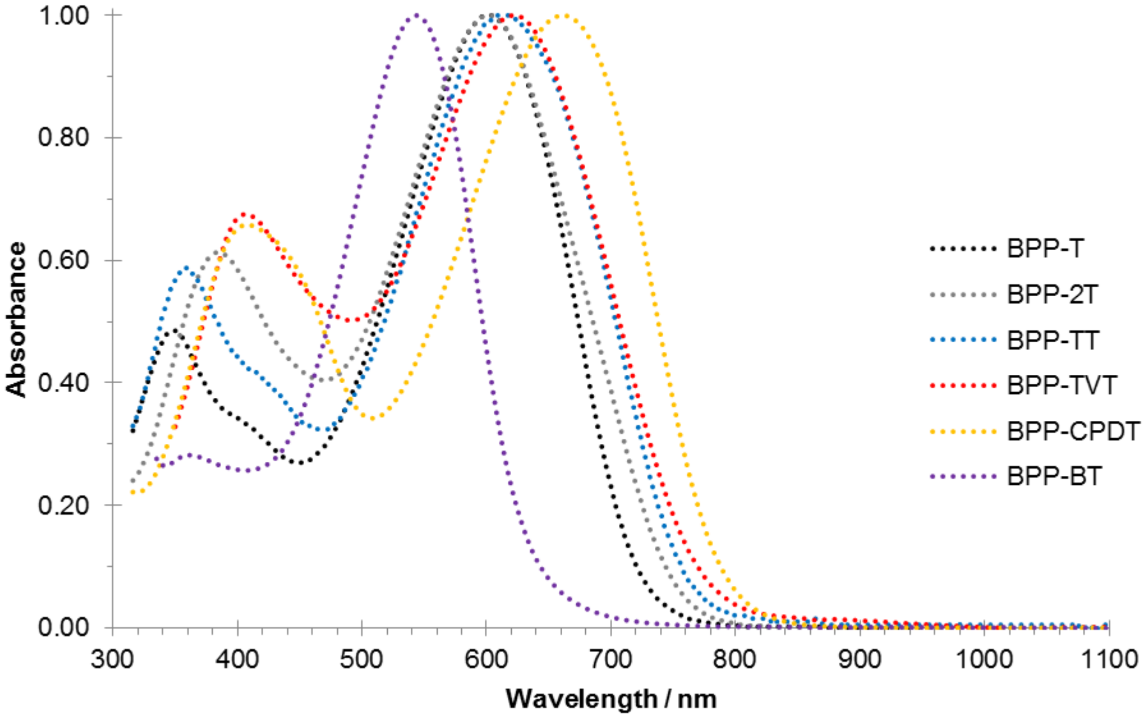
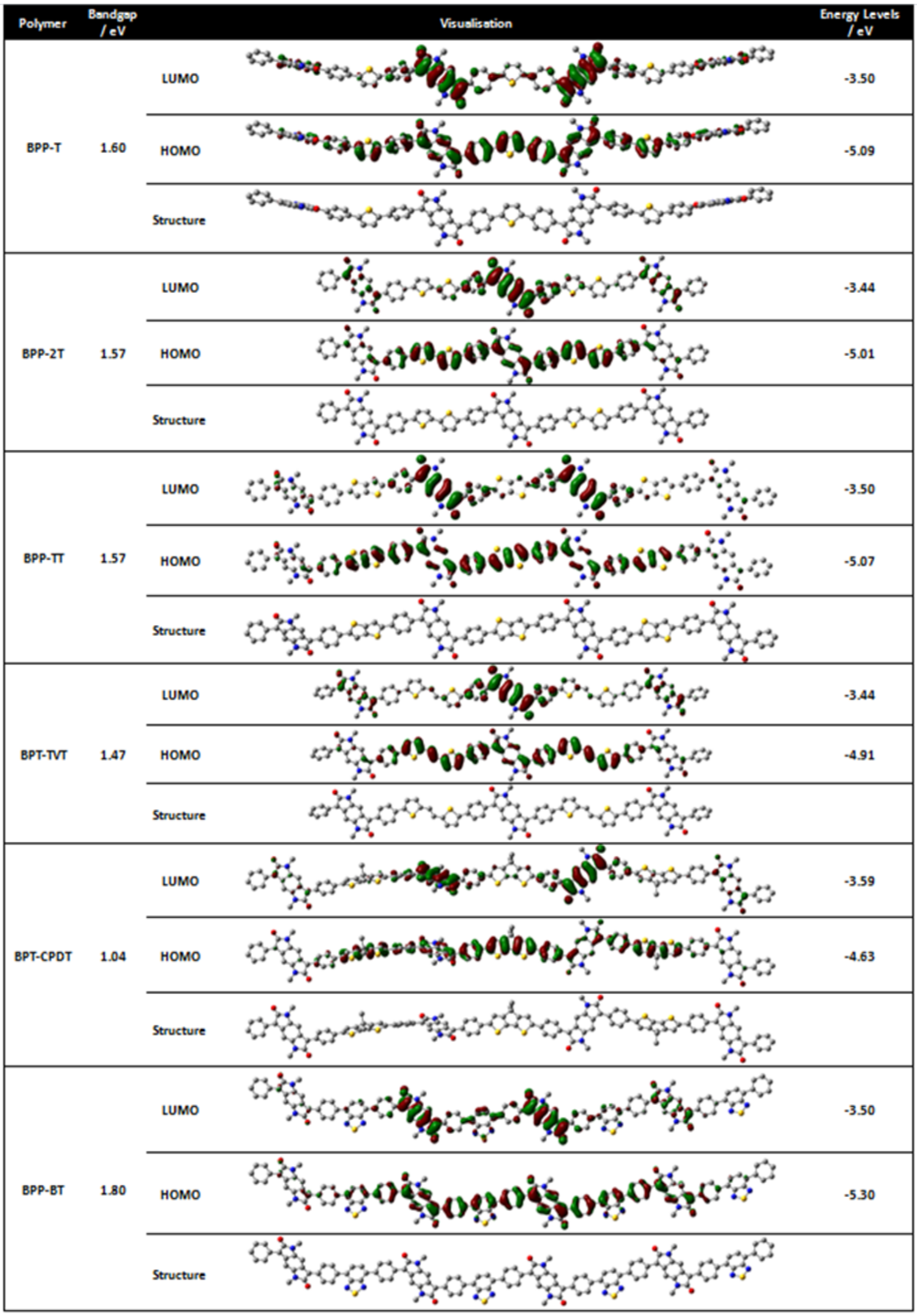


Figure S10. Normalised UV-Vis absorption spectra of the **BPP**-based copolymers: in solutions (dilute chlorobenzene).



Polymer	Bandgap / eV	Visualisation	Energy Levels / eV
BPP-T	1.60	LUMO	-3.50
		HOMO	-5.09
		Structure	
BPP-2T	1.57	LUMO	-3.44
		HOMO	-5.01
		Structure	
BPP-TT	1.57	LUMO	-3.50
		HOMO	-5.07
		Structure	
BPT-TVT	1.47	LUMO	-3.44
		HOMO	-4.91
		Structure	
BPT-CPDT	1.04	LUMO	-3.59
		HOMO	-4.63
		Structure	
BPP-BT	1.80	LUMO	-3.50
		HOMO	-5.30
		Structure	

Figure S11. Computational models of the **BPP**-based copolymers showing the energy minimised structures with *N*-methyl substitution and visualisation of the HOMO and LUMO energy distributions (hydrogens are omitted from view for clarity); the predicted HOMO and LUMO energy levels and bandgap are also quoted.

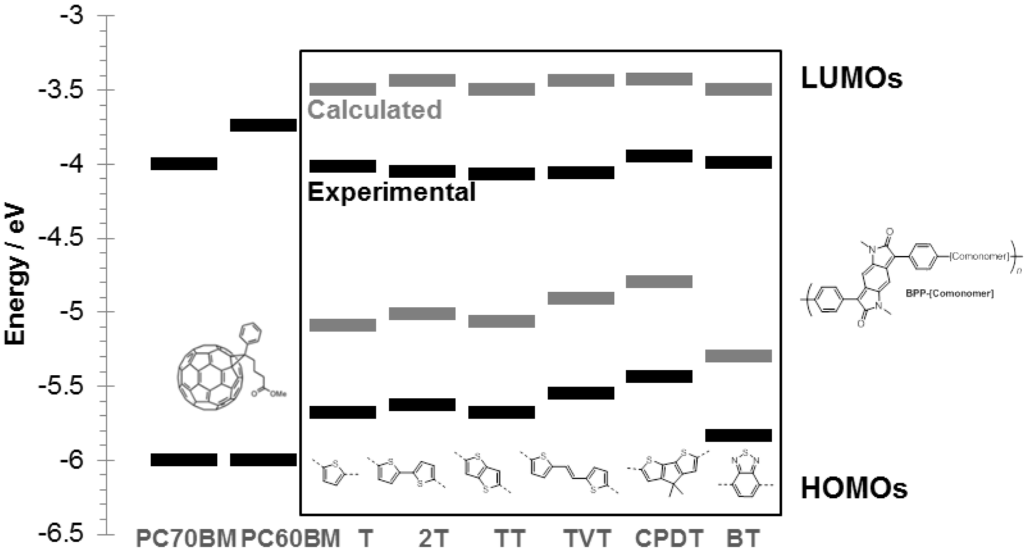


Figure S12. Comparison of HOMO and LUMO energy levels and bandgaps across the series of the **BPP**-based copolymers as calculated from computational models and found experimentally.

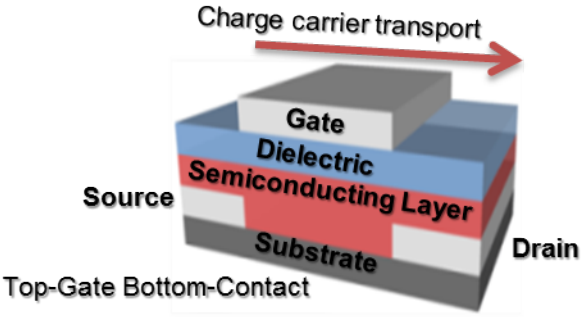


Figure S13. The top-gate, bottom-contact organic field effect transistor (OFET) architecture employed.

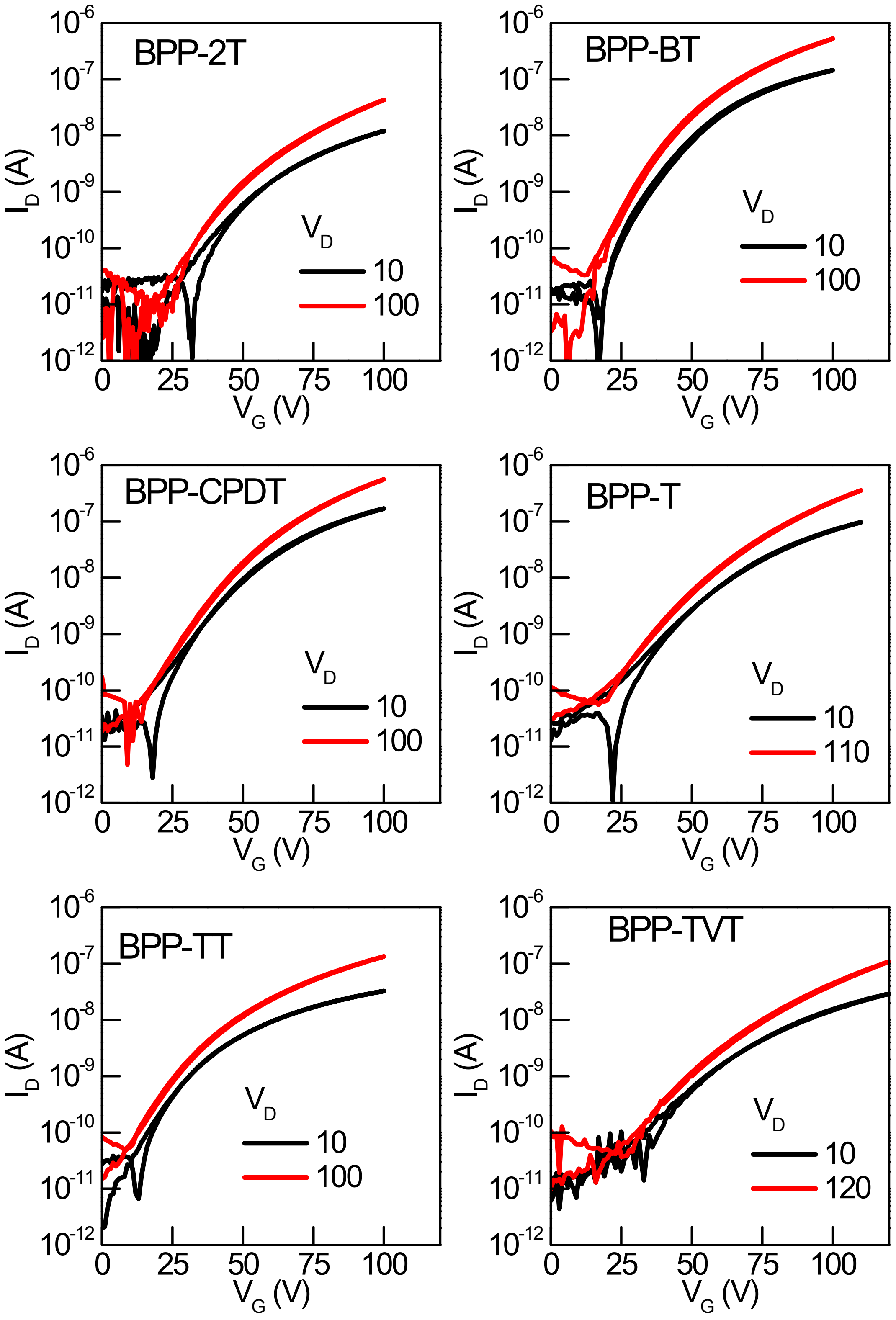


Figure S14. Transfer curves for the **BPP**-based copolymer field-effect transistor devices annealed at 100 °C (top-gate, bottom-contact architecture).

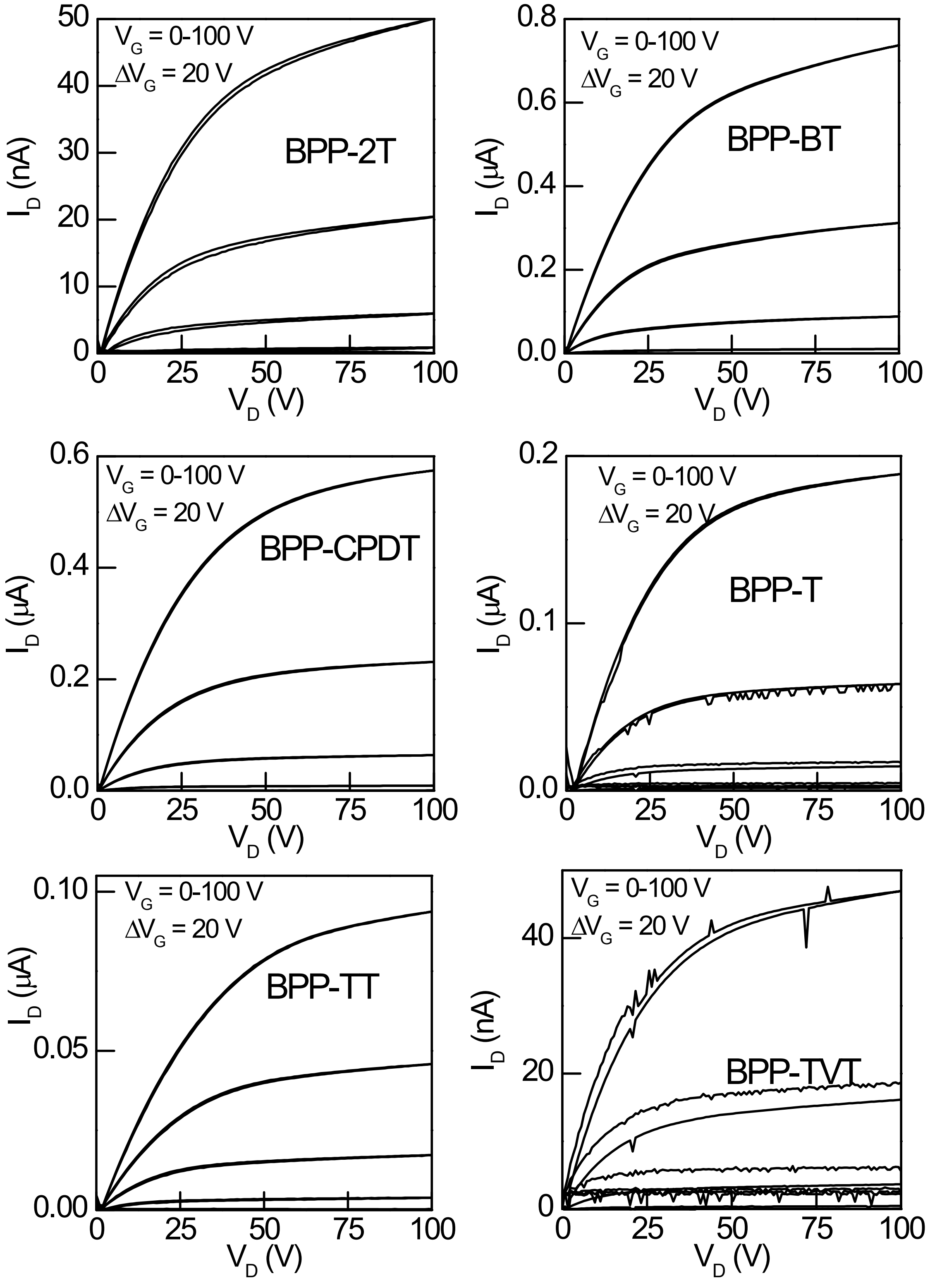


Figure S15. Output curves for the **BPP**-based copolymer field-effect transistor devices annealed at 100 °C (top-gate, bottom-contact architecture).

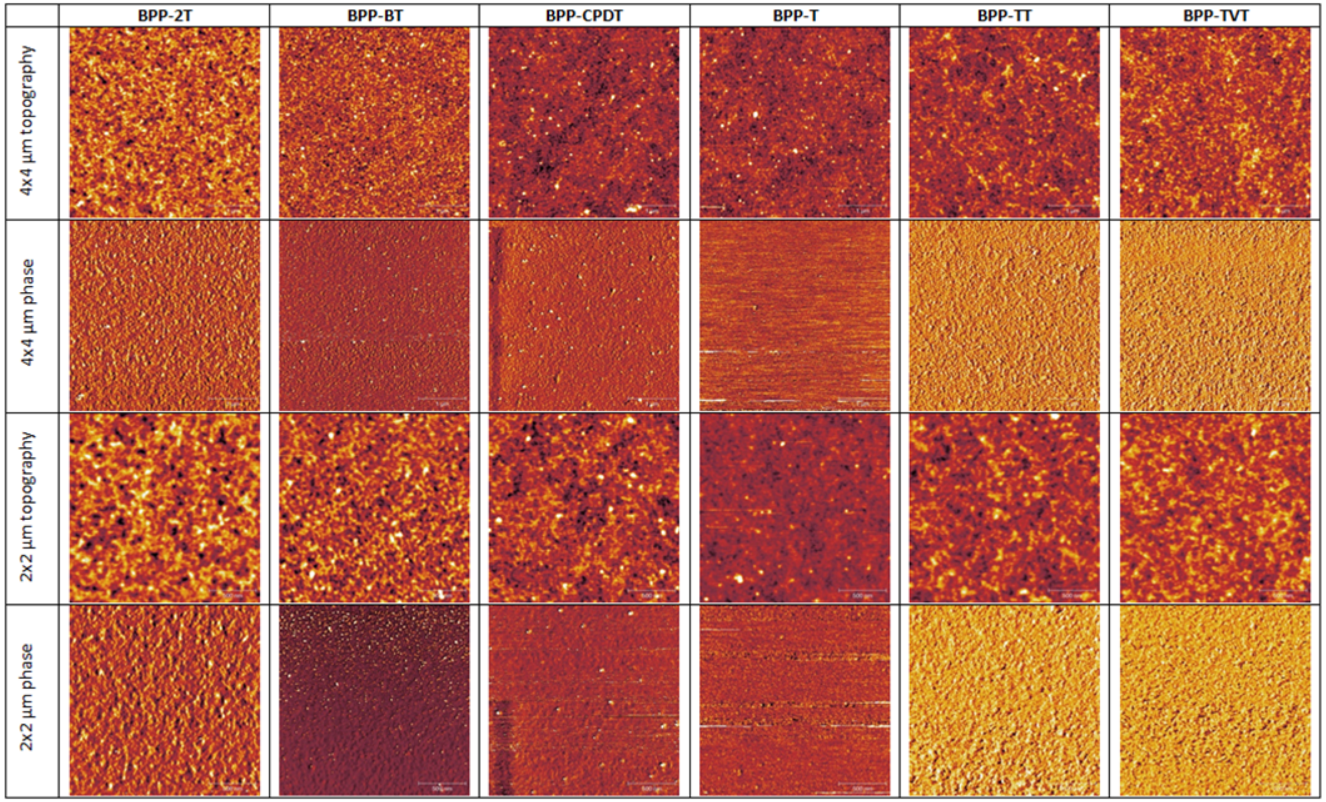


Figure S16. Atomic force microscopy (AFM) images of the **BPP**-based copolymer films akin to field-effect transistor devices (dried at 100 °C).

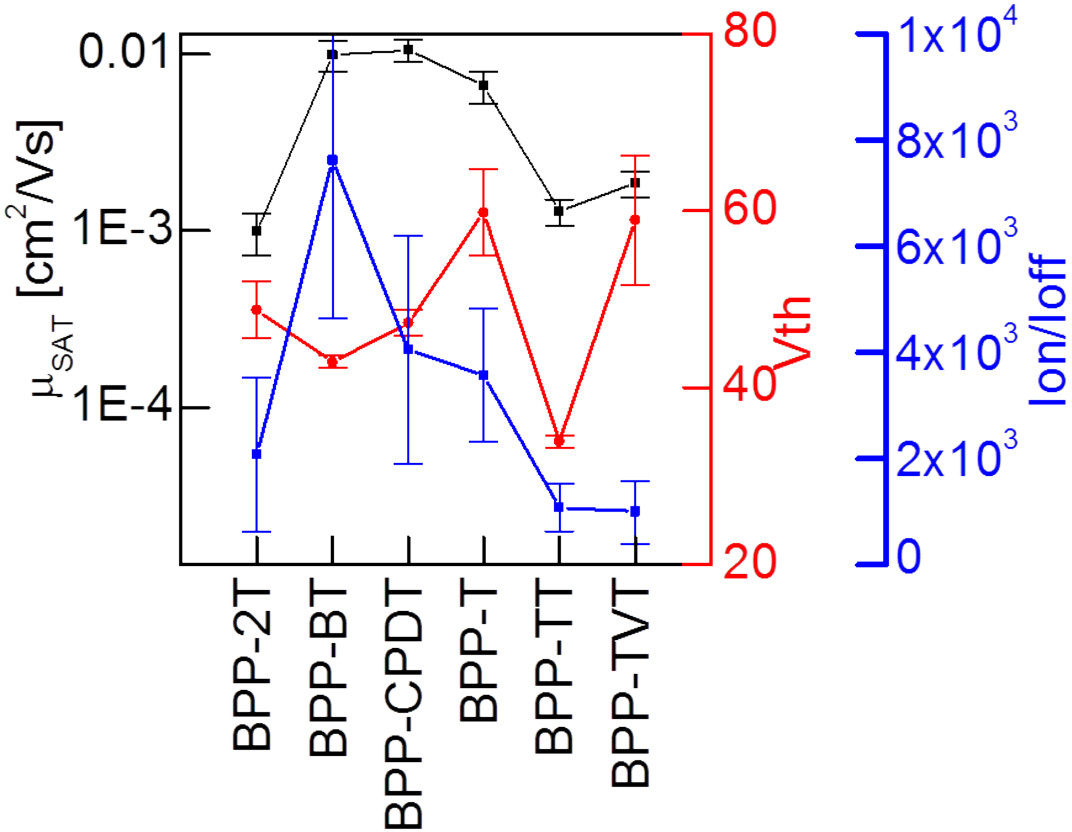
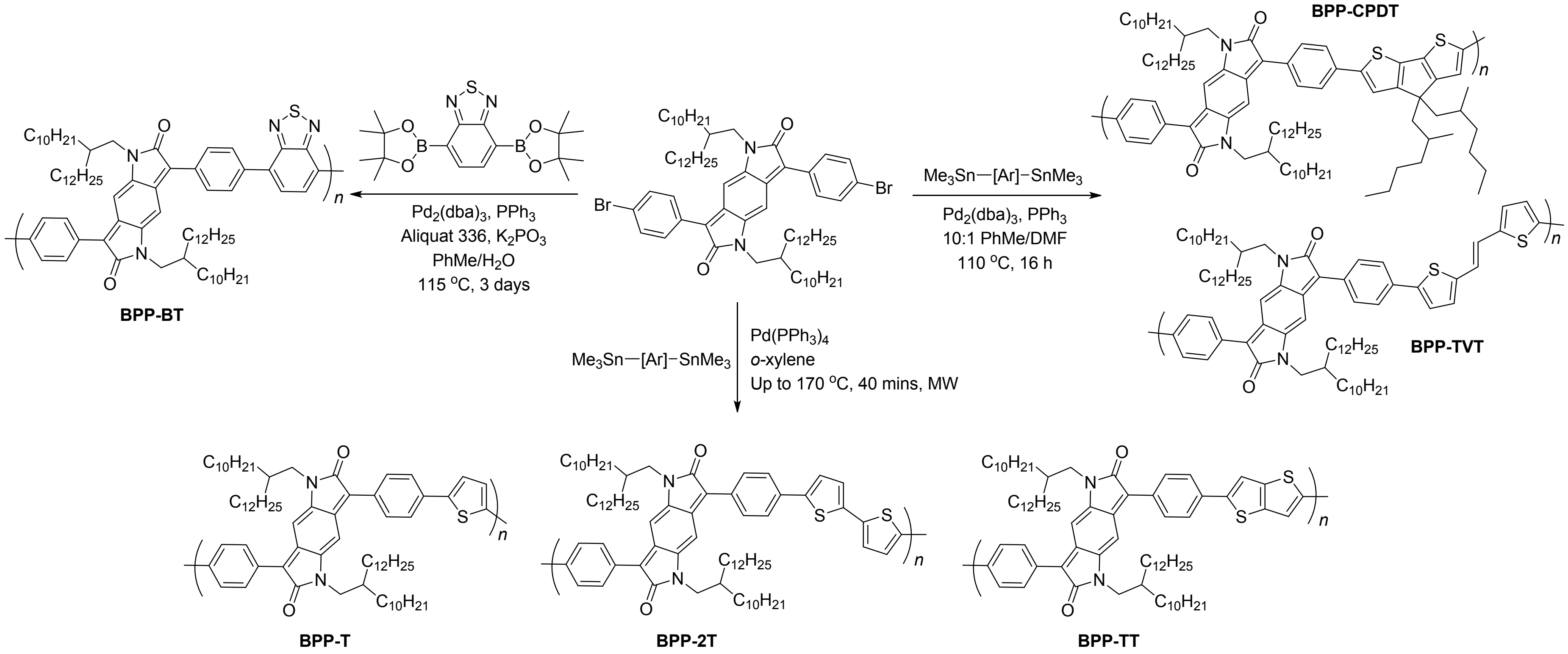


Figure S17. Comparison of electron mobilities (μ_{SAT} [cm^2/Vs]), threshold voltages (V_{th} [V]) and $I_{on/off}$ ratios for the **BPP**-based copolymer OFET devices annealed at 100 °C (top-gate, bottom-contact architecture).

Additional Schemes



Scheme S1. Synthesis of the phenyl-flanked benzodipyrrolidone-based (**BPP**) copolymers by palladium catalyzed cross-coupling methodology.